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REPORT DOCUMENTATION PAGE

AD-A218 715

1b. RESTRICTIVE MARKINGS

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PERFORMING ORGANIZATION REPORT NUMBER(S)	5. MONITORING ORGANIZATION REPORT NUMBER(S)

NAME OF PERFORMING ORGANIZATION	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION
Rensselaer Polytechnic Institute		ONR

ADDRESS (City, State, and ZIP Code)	7b. ADDRESS (City, State, and ZIP Code)
Department of Chemistry Troy, New York 12180-3590	Department of Navy Arlington, VA 22217

NAME OF FUNDING/SPONSORING ORGANIZATION	8b. OFFICE SYMBOL (If applicable)	9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
ONR		Contract # N00014-85-K-0632

ADDRESS (City, State, and ZIP Code)	10 SOURCE OF FUNDING NUMBERS			
Department of Navy Arlington, VA 22217	PROGRAM ELEMENT NO	PROJECT NO.	TASK NO	WORK UNIT ACCESSION NO

TITLE (Include Security Classification)
Comparison of Isoelectronic Aluminum-Nitrogen and Silicon-Carbon Double Bonds Using Valence Bond Methods

PERSONAL AUTHOR(S)
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a. TYPE OF REPORT	13b. TIME COVERED		14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Publication	FROM ____	TO ____		21

SUPPLEMENTARY NOTATION

COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	AlN Precursor, Dimethylaluminum Amide, AlN Double Bonds, Molecular Geometry Calculations

ABSTRACT (Continue on reverse if necessary and identify by block number)

Dimethyl-aluminum amide $((CH_3)_2AlNH_2)$ is a postulated intermediate in the reaction between trimethyl aluminum $((CH_3)_3Al)$ and ammonia to form aluminum nitride. Results of geometry optimization calculations for $(CH_3)_2AlNH_2$, H_2AlNH_2 and isoelectronic H_2SiCH_2 (silaethylene) are presented. Each of these has a planar equilibrium skeleton with C_{2v} symmetry. Geometry optimizations were carried out using Generalized Valence Bond Perfect-Pairing (GVB-PP) wave functions. Al=N bond distances of 1.78 and 1.80 Å are predicted for the dihydro- and dimethylaluminum amides, respectively, slightly longer than the optimized Si=C bond distance in silaethylene (1.74 Å). Al=N bond distances in these compounds are fitted into a phenomenological correlation established by Haaland which relates the covalent:dative character of such a bond to the bond distance. We compare the Al=N and Si=C bonds in the shapes of the GVB-PP orbitals representing them and in their predicted dipole moments.

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SECURITY CLASSIFICATION OF THIS PAGE

Unclassified

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January 15, 1990

Comparison of isoelectronic aluminum-nitrogen and silicon-carbon double bonds using valence bond methods

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Abstract

Dimethyl-aluminum amide ((CH_3)$_2$AlNH$_2$) is a postulated intermediate in the reaction between trimethyl aluminum ((CH_3)$_3$Al) and ammonia to form aluminum nitride. Results of geometry optimization calculations for (CH_3)$_2$AlNH$_2$, H_2AlNH$_2$ and isoelectronic H_2SiCH$_2$ (silaethylene) are presented. Each of these has a planar equilibrium skeleton with C_{2v} symmetry. Geometry optimizations were carried out using Generalized Valence Bond Perfect-Pairing (GVB-PP) wave functions. Al=N bond distances of 1.78 and 1.80Å are predicted for the dihydro- and dimethyl-aluminum amides, respectively, slightly longer than the optimized Si=C bond distance in silaethylene (1.74Å). Al=N bond distances in these compounds are fitted into a phenomenological correlation established by Haaland which relates the covalent:dative character of such a bond to the bond distance. We compare the Al=N and Si=C bonds in the shapes of the GVB-PP orbitals representing them and in their predicted dipole moments.

Introduction

Oligomeric alkylaluminum amides[1-9] $(R_2AlNR'R'')_n$ have recently been the subject of renewed interest owing to their potential utility as precursors to aluminum nitride[8, 10, 11] (AlN). In 1939 Wiberg[12] elucidated a series of reactions involving the synthesis of methylaluminum amides and imides which generate aluminum nitride when heated as shown below:

$$Me_3Al + NH_3 \rightarrow Me_3Al{:}NH_3 \rightarrow (Me_2AlNH_2)_{2 \text{ or } 3} \rightarrow (MeAlNH)_n \rightarrow AlN. \quad (1)$$

The rational design of precursors to aluminum nitride requires a detailed knowledge of the intermediate steps which occur in the sequence of reactions in (1) above; in particular, in this work we are interested in the first methane loss step which results in formation of aluminum amides. Interrante et al.[8] have studied the thermodynamic, kinetic and mechanistic aspects of the reaction:

$$Me_3Al + NH_3 \rightarrow Me_3Al{:}NH_3 \rightarrow 1/3(Me_2AlNH_2)_3 + CH_4 \quad (2)$$
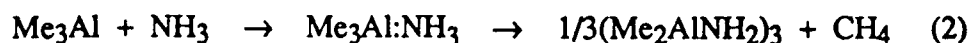
and have proposed monomeric Me_2AlNH_2 as an intermediate which participates as a catalyst in methane loss from the Lewis acid-base adduct Me_3AlNH_3[9]. This species may also be present as a gas phase, or surface-adsorbed species in the chemical vapor deposition of AlN[13] and in solution during the thermal equilibration of the more thermodynamically stable trimeric species $(Me_2AlNH_2)_3$[14]. The theoretical studies reported here pursue the question of the structure and bonding in Me_2AlNH_2. We compare bonding and the predicted structure of Me_2AlNH_2 to two related molecules - H_2AlNH_2, and H_2SiCH_2 (silaethylene).

The strong tendency of alkylaluminum amides to oligomerize results in formation of Lewis acid-base complexes of the type $(R_2AlNR'R'')_n$, whose structures consist of four or six membered aluminum-nitrogen rings whose size (n= 2 or 3) depends largely on the particular groups attached to Al or N. Heating the aluminum amides to moderate temperatures in solution results in elimination of alkane and formation of alkylaluminum imides $(RAlNR')_n$[15-17]. Imide aggregates

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with n up to 16 have been reported[17] and structures are known for compounds where n= 4[16], 6-8[17].

A recent review of dative bonds to main group elements[18] has collected a body of information on dative bonds; the data show that distances and strengths of dative bonds vary to a much larger degree than covalent bonds for a particular pair of atoms and that they have large inductive effects, especially at the acceptor atom. Aluminum nitrogen bond lengths in the imide compounds above and in the oligomeric amides fall into the range 1.89-1.96Å[17]. Recently, the synthesis and structure of the first aluminum nitrogen compound with multiple Al-N bonds was reported[19]. This compound, $[MeAlN(2,6-iPr_2C_6H_3)]_3$, is an $(AlN)_3$ analog of borazine whose structure consists of a planar ring of alternating Al and N atoms with an average AlN (multiple) bond distance of 1.78Å and bond angles which deviate by ~5° from 120°. In our discussion we show that Al=N bond lengths of the amide compounds reported here fit into a correlation between covalent/dative character and bond length already established by Haaland[18]. We also make a comparison between the Al=N bond in H_2AlNH_2 and the Si=C bond in H_2SiCH_2. The Si=C bond distance was the subject of controversy until 1985 because of conflicting electron diffraction data[20] and results of *ab initio* calculations[21] which determined the Si=C bond length in 1,1-dimethylsilaethlene to be 1.83 and ~1.70Å, respectively. X-ray crystallographic data for a compound with a bond distance of 1.702[22(a)] and a microwave study of 1,1-dimethylsilaethylene[22(b)] are in agreement with the *ab initio* results and have resolved the conflict; the generally accepted Si=C bond distance in silaethylenes is now around 1.70Å.

In this work, geometries of the three compounds mentioned above were optimized using the Generalized Valence Bond Perfect-Pairing (GVB-PP) method which assumes the strong orthogonality and perfect-pairing (SOPP) restrictions on the wave function (see appendix). In each case six valence electron pairs were correlated (two pairs in the Al=N or Si=C bonds and four pairs in the remaining bonds to hydrogen or methyl groups) and the remaining valence electron pairs and core electrons were treated at the Hartree-Fock (HF) level.

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Results

Me_2AlNH_2

Two conceivable geometries for Me_2AlNH_2 are a planar structure with C_{2v} symmetry or a bent structure with C_s symmetry depending on whether an Al=N double bond *or* a single bond and an unbonded lone pair is the most energetically favorable bonding situation. GVB-PP geometry optimization showed that the equilibrium geometry was in fact the planar structure; equilibrium bond distances and angles and the total energy are given in Table 1 and details of the basis sets used are given in appendix A. A GVB-PP calculation on Me_2AlNH_2 in which the Al-N bond distance was 1.95Å and the bond angles about the nitrogen atom were $110°$ yielded a total energy 10.16 kcal mol^{-1} *higher* than the equilibrium geometry. There was no local minimum in total energy for a structure with C_s symmetry since a geometry optimization calculation with this starting geometry collapsed rapidly to the planar structure obtained above. The Al-N equilibrium bond length of 1.80Å is considerably shorter than Al-N single bond distances found in the oligomerized amide which has a single Al-N bond distance of 1.935Å[8].

A schematic representation and contour plots of the self-consistent GVB-PP orbitals for the Al-N bonds in Me_2AlNH_2 are shown in Fig. 1 (a, b). An explanation for the short Al=N bond distance becomes clear by examining the orbitals. The bond is represented as two radially correlated pairs localized on the nitrogen atom forming dative bonds to the Al atom[23]. Contour plots of the GVB-PP orbitals representing the N-H and Al-C bonds constructed in the molecular plane are shown in Fig. 1 (c, d). Note that in each case there is one orbital localized on either atom participating in the bond and that orbitals localized on first row elements are much more contracted than those localized on second row atoms. The predicted dipole moment is 0.9 Debye *with the negative pole towards Al.*

H_2AlNH_2

The equilibrium structures of dimethyl-aluminum amide and dihydro-aluminum amide (Table II) are very similar. The Al=N bond distance is 0.01Å shorter in the dihydrogen compound

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and the N-H bonds are predicted to be the same length. Thus there are only minor substituent effects on structure for H compared to CH_3. Contour plots of the GVB-PP orbitals representing the Al=N, Al-H and N-H bonds are shown in Fig. 2. The only major difference in orbital contours is found for the Al-H bonds. The predicted dipole moment is 1.3 Debye *with the negative pole towards Al.*

H_2SiCH_2

Silaethylene is unstable with respect to dimerization to the disila-cyclobutane; in an inert gas matrix dimerization proceeds at temperatures above 10K[24]. Theoretical predictions for the Si=C bond distance in both silaethylene[21(a-e, g, i)] and dimethylsilaethylene[21(b)] are in the range 1.692-1.728Å in silaethylene and ~1.692Å in 1,1-dimethylsilaethylene; electron withdrawing substituents on the Si atom shorten the Si=C bond (by -0.034Å for F[21(d)]) and the opposite effect is predicted for electron withdrawing substituents on C (by +0.021Å for F[21(d)]).

Our optimized geometry (Table III) for H_2SiCH_2 predicts an Si=C bond distance of 1.74Å[25]. There are two alternative descriptions for double bonds using the present GVB-PP wave function, either there are two equivalent bent bonds (or Ω bonds), or there is one σ and one π bond. The Ω bond description is more appropriate for comparison to the bonding in the aluminum amides because then the descriptions are equivalent, *i.e.* we use bent bonds for comparison in both cases. Descriptions in terms of $\sigma\pi$ or Ω bonds differ in total energy by a small amount; for ethylene[26] the Ω bond description is 3.45 kcal mol^{-1} higher in total energy but for silylene[27] (Si_2H_4) the Ω bond description is 0.8 kcal mol^{-1} *lower.* However, both of the calculations mentioned above applied the SOPP restrictions to the GVB wave function (as does our work) which has been shown to be *biased against* a lower total energy for Ω bonds in a number of molecules[28] including ethylene[26]. In fact in all multiply bonded cases studied, the Ω bonded description was *lower* in energy when the SOPP restrictions were relieved. Given the energetic comparison above of $\sigma\pi$ and Ω descriptions for ethylene and silylene, it is not surprising to find that the relative stability of the $\sigma\pi$ and Ω bonded descriptions of silaethylene is intermediate

between the relative stabilities of these descriptions for ethylene and silylene; the Ω bonded description of silaethylene is 2.42 kcal mol^{-1} *higher* than the $\sigma\pi$ description (the comparison was made at the $\sigma\pi$ equilibrium geometry). We anticipate on the basis of previous experience that the removal of the SOPP restrictions on the wave function will give the Ω bond description the lower energy. Contour plots of GVB-PP orbitals representing the Ω bond orbitals in silaethylene are shown in Fig. 3 (a, b) and plots representing the Si-H and C-H bonds are shown in Fig. 3 (c, d). In contrast to the orbitals in the Al=N bond, there is one orbital localized on each atom in the Si=C bond. The $\sigma\pi$ orbitals representing the Si=C double bond are shown in Fig. 4. The predicted dipole moment is +0.6 Debye *with the negative pole towards C*.

Discussion

We may naively regard the Al=N and Si=C bonds as being composed of one dative plus one covalent bond[29] and two covalent bonds, respectively. However, in order to know more about bonding in a compound such as Me_2AlNH_2 it is useful to make comparisons to other AlN compounds with a variety of bonding modes and to silaethylene which is an approximation to the 'covalent limit' for such bonds; dative bonds have a much greater variation in length than covalent bonds and have strengths up to half the covalent bond strength[18]. Electron withdrawing groups bonded to the acceptor atom tend to shorten and strengthen dative bonds while electron donors have the opposite effect - this is the inductive effect.

Bond Distances

Dative bond distances in alane complexes with trimethyl amine respond to groups with large inductive effects: the (purely dative) bond lengths in $Me_3N{\rightarrow}AlX_3$ are 1.96, 2.06 and 2.10Å for X=Cl[30], H[31] or CH_3[32], respectively. Bonds with mixed covalent/dative character (*i.e.* those which are drawn as canonical structures where a particular bond is dative in one structure but covalent in an alternative one, such as a bridging NH_2 group) are shorter: in ref. 18 a correlation between bond length and the covalent/dative character of a series of compounds is demonstrated. For example, in the adducts just mentioned the covalent:dative ratio is 0:1 and a typical bond length

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(when no large inductive effect groups are present) is 2.06Å; in the trimeric amide $(Me_2AlNH_2)_3$ the ratio is 1:1 and the bond length is 1.93Å[8]; in the polyimide $(HAlNiPr)_4$[16] the covalent:dative ratio is 2:1 and it has a bond length of 1.91Å; in crystalline AlN[33] the covalent:dative ratio is 3:1 and the bond length is 1.88Å.

These compounds all have single Al-N bonds and the bond length decreases as the covalent:dative ratio increases. In the compounds studied in this work the covalent:dative ratio is 1:1 but the Al=N bond order is formally 2. We should like to know the distances of single Al-N and double Al=N bonds with covalent:dative ratios of 1:0 and 2:0, respectively. In a recent review article on dative bonding[18] the terminal NMe_2 groups in dimeric $(Me_2N)_3Al$ are assigned a covalent:dative ratio of 1:0, *i.e.* they are regarded as single, purely covalent bonds. This assumes a maximum of four bonds to an Al atom and that the nitrogen lone pairs on the terminal NMe_2 groups are not involved in the bond. However, second row elements bonded to electronegative elements are frequently hypervalent, *i.e.* there are more than four bonds to the hypervalent atom. This has recently been demonstrated via GVB-PP calculations for sulfur dioxide and related molecules[34]. We expect that the Al=N bond to the terminal NMe_2 groups is actually a double bond similar to the bond in H_2AlNH_2 or Me_2AlNH_2 which explains the similarities in Al=N bond distances: 1.81[35], 1.78 and 1.80Å, respectively. In agreement with this conclusion, a higher bond order (~2) than expected for this compound from MO calculations was reported recently[36]. Thus we still require AlN reference distances for purely covalent single and double bonds. Instead we choose the Si-C (1.875Å) and Si=C (1.702Å) distances in $SiMe_4$[37] and $Me_2SiC(SiMe_3)(SiMetBu_2)$[22(a)] as experimental reference bond distances. The 1:0 covalent:dative Si-C bond is, as should be expected, only slightly shorter than the predominantly covalent Al-N bond in crystalline AlN (1.88Å)[33]. Thus the trimeric amide $(Me_2AlNH_2)_3$ which has similar (methyl) inductive effects to $SiMe_4$ but a covalent:dative ratio of 1:1 instead of 1:0 has an (experimental) Al-N distance of 0.06Å longer than the $SiMe_4$ reference single bond and the monomeric amide (Me_2AlNH_2), with a covalent:dative ratio of 1:1 has a (calculated) bond distance 0.06Å longer than the calculated reference distance in silaethylene (this work) with a 1:0 ratio.

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Again, the $(AlN)_3$ borazine analog[20] mentioned in the introduction has a covalent:dative ratio of 2:1 and a formal bond order of 1.5; on account of its smaller bond order we might expect the Al-N distance to be greater than in Me_2AlNH_2 but on account of its covalent:dative ratio we might expect the bond to be shortened with respect to Me_2AlNH_2. The experimental value of 1.78Å[20] is actually slightly less than our predicted value for Me_2AlNH_2.

Substituent Inductive Effects

The electron donating effect of methyl substituents on Al leads to a smaller dipole in Me_2AlNH_2 (0.9D) compared to H_2AlNH_2 (1.3D). This is also reflected in the shorter Al=N bond in H_2AlNH_2. Contours of the orbitals representing the Al=N and N-H bonds in Me_2AlNH_2 and H_2AlNH_2 do not differ appreciably, however. The contours themselves are almost congruent and the only major changes in orbital contours are found in the bond that is being replaced, *i.e.* the Al-C bond. Hence, judging by orbital shapes and changes in bond length, there are only minor substituent effects on the Al-N bond evident from calculations when the methyl substituents are replaced by hydrogen.

Covalent vs Covalent/Dative Bonding

Comparing the Al=N and Si=C orbital shapes in H_2AlNH_2 and H_2SiCH_2 we see that while, in the amide both orbitals in the pairs forming the Al=N bond are chiefly localized on the N atom, in silaethylene there is one orbital chiefly localized on Si and one localized on C, although the pair is distorted towards C. In this case no pairs have to be donated in order to achieve a bond and so the dipole lies in the direction of the more electronegative element - carbon. The bond length is only 0.045Å shorter than the Al=N bond in H_2AlNH_2.

Appendix: Computational Details

GVB-PP calculations within the Strong Orthogonality and Perfect Pairing (SOPP) approximations[38] were carried out using the GVB2P5[39] and GAMESS[40] programs. The GAMESS program was employed for geometry optimizations. Polarized double-zeta (DZ) basis sets of Huzinaga[41] using the [11s7p/6s4p] contractions of Dunning[41] were used for aluminum and

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silicon atoms. The *d* polarization function exponents for Al and Si were 0.25 and 0.32; no polarization functions were employed on the C or N atoms in geometry optimizations. The Huzinaga valence DZ basis[41] sets (using the Dunning [9s5p/3s2p] contraction[41]) were used for carbon and nitrogen. The hydrogen atom basis set was the unscaled [3s/2s] contraction of the basis of Huzinaga[41].

Acknowledgements

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Figure Captions

Fig. 1

Contour plots of GVB-PP orbitals for Me_2AlNH_2. (a), (b) orbitals representing the Al=N bond perpendicular to the molecular plane; (c) orbitals representing the N-H bond and (d) orbitals representing the Al-C bond in the molecular plane. Contours are plotted at 0.04 a.u. intervals in all figures.

Fig. 2

Contour plots of GVB-PP orbitals for H_2AlNH_2. (a), (b) orbitals representing the Al=N bond perpendicular to the molecular plane; (c) orbitals representing the N-H bond and (d) orbitals representing the Al-H bond in the molecular plane.

Fig. 3

Contour plots of GVB-PP orbitals for the Ω bond representation of H_2SiCH_2. (a), (b) orbitals representing the Si=C bond perpendicular to the molecular plane; (c) orbitals representing the C-H bond and (d) orbitals representing the Si-H bond in the molecular plane.

Fig. 4

Contour plots of GVB-PP orbitals for the $\sigma\pi$ bond representation of H_2SiCH_2. (a) π bond orbitals and (b) σ bond orbitals representing the Si=C bond perpendicular to the molecular plane.

Table 1

Bond distances and angles for Me_2AlNH_2.

Bond	Length (Å)	Angle	Degrees
Al-N	1.797	C-Al-N	119.4
Al-C	1.994	C-Al-C	121.2
N-H	1.026	H-N-H	110.3
C-H	1.096	H-Al-C	124.9

E = -376.834 93 H

Table 2

Bond distances and angles for H_2AlNH_2.

Bond	Length (Å)	Angle	Degrees
Al-N	1.785	H-Al-N	118.5
Al-H	1.606	H-Al-H	123.1
N-H	1.026	H-N-H	110.3
		H-Ṅ-Al	124.8

E_σ= -298.776 04 H

Table 3

Bond distances and angles for H_2SiCH_2.

Bond	Length (Å)	Angle	Degrees
Si-C	1.740	H-Si-C	115.0
Si-H	1.495	H-Si-H	122.5
C-H	1.102	H-C-H	115.5
		H-C-Si	122.2

$E_{\sigma\pi} = -329.112\ 34\ H$[1]

$E_{\Omega,pol} = -329.116\ 34\ H$[2]

$E_{\sigma\pi,pol} = -329.121\ 32\ H$[3]

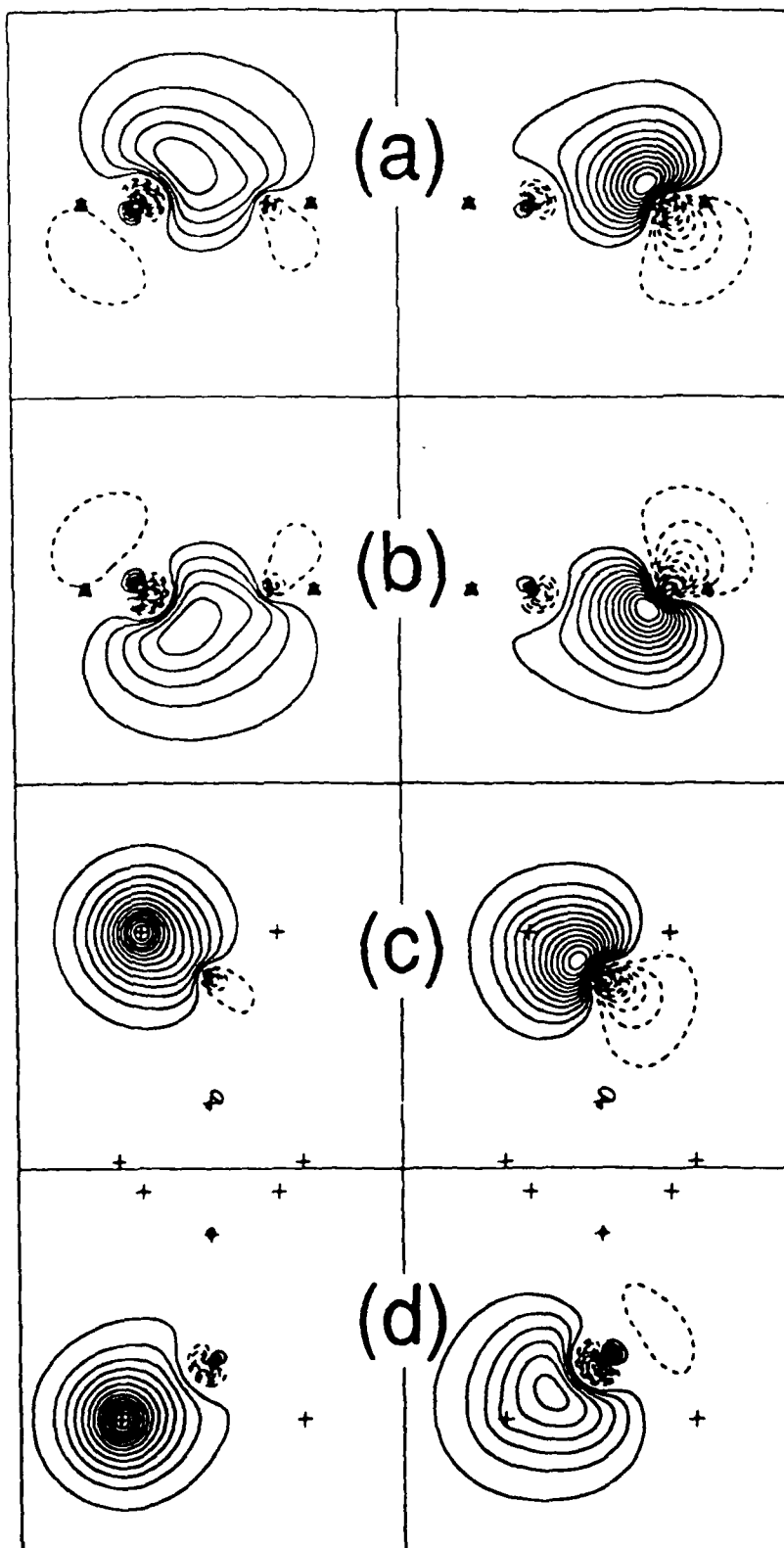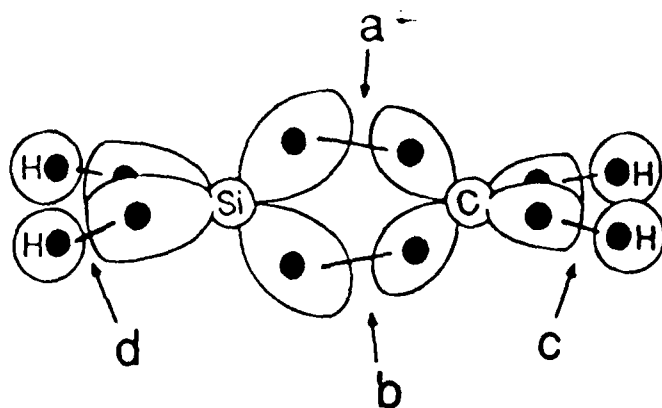[1] $\sigma\pi$ double bond; basis set includes polarization function on Si only.

[2] Ω double bond; basis set includes polarization function on Si and C; Si=C bond distance: 1.735Å.
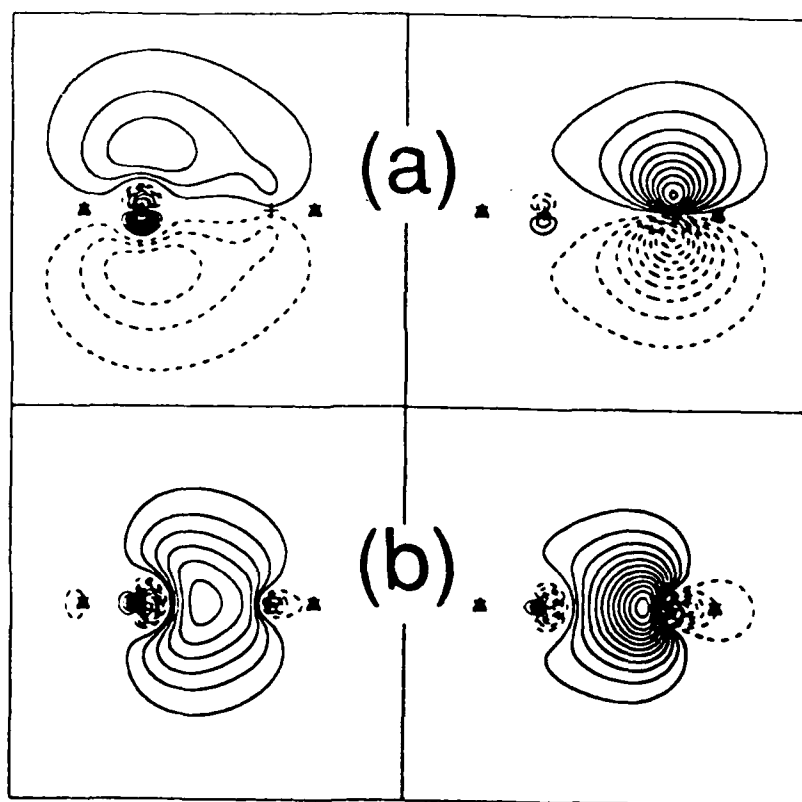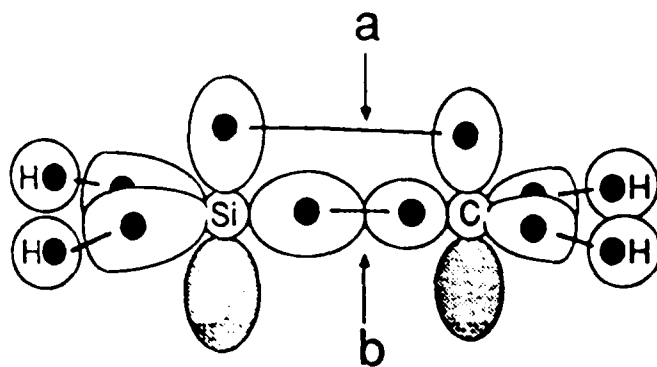
[3] $\sigma\pi$ double bond; basis set includes polarization function on Si and C; Si=C bond distance: 1.735Å.

CH₃

CH₃

Al

a

N

H

H

b

c

d

(a)

(b)

(c)

(d)

Lynnm et al.

Fig 1

Lynam et al.
Fig 2

(a)

(b)

(c)

(d)

Lynam et al.

Fig 3

a

b

(a)

(b)